

Final Report for Period: 08/2008 - 07/2009

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Principal Investigator: El-Sayed, Mostafa A.

Award ID: 0554668

Organization: GA Tech Res Corp - GIT

Submitted By:

El-Sayed, Mostafa - Principal Investigator

Title:

The Stability of Colloidal Metallic Nanoparticles in Reactive Chemical Environments

Project Participants

Senior Personnel

Name: El-Sayed, Mostafa

Worked for more than 160 Hours: Yes

Contribution to Project:

Post-doc

Graduate Student

Undergraduate Student

Technician, Programmer

Other Participant

Research Experience for Undergraduates

Organizational Partners

Other Collaborators or Contacts

Activities and Findings

Research and Education Activities:

1. Trying to synthesize monodispersed catalytic nanoparticles in colloidal solutions:
 - a. Trying to modify the colloidal methods to synthesize important nanoparticles of different shapes.
 - b. Another method we are trying involves combining lithographic techniques known to produce highly mono-dispersed structures and using femtosecond laser pulses to photo-thermally eject them. Successful preparation was accomplished. The characterization of the particles produced is now in progress.
2. Trying to understand the fundamentals of nanocatalysis of particles of different sizes and shapes.
3. Is colloidal catalysis occurring on the surface of the nanoparticle or by leached atoms in solution?

A number of experiments have been carried out to answer this important question. No confirmed results have been reported on this. It was very difficult to distinguish between the two mechanisms. It was difficult to make a membrane that can effectively filter out the nano-particles. It is very possible both mechanisms are taking place as the atoms on the surface of the nano-particle are very unstable. Thus, the competition between the reaction of the added reactants on the surface with one another and the reaction of one or both of the reactants (or the solvent) with the surface atoms will determine the exact mechanism involved.

4. Reviews are written which examine the good and the bad about colloidal nanocatalysis in order to educate researchers in the field about its rapid progress

5. Trying to attract minorities to our group both on the graduate and on the undergraduate levels.

Findings:

1. we can combine electron beam Lithography and femto-second lasers to prepare colloidal nanoparticles of very narrow size distribution is a new technique in nanosynthesis (A paper is published on this)

2. We began detailed examination of the molecular mechanism of nanocatalysis. We found a new intermediate that contains atoms from the nanocatalyst. This might change the definition of some nanocatalysis :

Reaction of platinum nanocatalyst with the ferricyanide reactant to produce Prussian Blue analog complexes

M. A. Mahmoud, M. A. El-Sayed*

(Journal of Physical Chemistry C (2007), 111(46), 17180-17183.)

Abstract

The field of catalysis with colloidal nanoparticles is in its infancy. The question of whether the catalysis occurs on the surface of the nanoparticle (thus heterogeneous) or homogeneously in soln. using a complex made by the nanoparticle is now being debated. Thus, the mol. mechanism of nanocatalysis has not been studied in detail. The first step in this effort is to study the mol. mechanism of the reaction of each reactant with the nanoparticle. This letter is an effort in this direction. A great deal of research has used platinum nanoparticles to catalyze electron-transfer reactions such as that between thiosulfate and hexacyanoferrate(III). We monitored this reaction in detail using optical, Raman and IR spectroscopies. By increasing the reaction time, two sequential dominant species are formed. The first one is found to have spectral signatures of a Prussian Blue analog with a structure of $K[Pt^{III}Fe^{III}(CN)_6]$. With increasing time, the intensity of the spectrum of this complex is found to decrease, whereas a spectrum similar to that of $[Pt^{IV}Fe^{II}(CN)_6]$ increased. A mechanism for the formation of these metal-mixed valency Prussian blue analogs is given.

3. We just published an ACS Communication reporting on the synthesis of a multiarmed (over 40 arms) platinum single Nanocrystal with high catalytic activities:

A New Catalytically Active Colloidal Platinum Nanocatalyst: The Multi-armed Nanostar Single Crystal

Mahmoud A. Mahmoud¹, Christopher E. Tabor¹, Mostafa A. El-Sayed^{1,*}, Yong Ding², and Zhong Lin Wang²

Communication ; Journal of the American Chemical Society (2008), 130(14), 4590-4591.

Abstract

Nano-catalysts that possess large amts. of atoms on sharp corners and edges and high indexed sites are known to be more catalytically active. We report here on a novel yet simple method to synthesize in large yields a very active platinum nanocatalyst; the multiarmed nanostar single crystal. We utilize a seed mediated method using tetrahedral nanoparticles that are also synthesized by a new and simple technique. High-resoln. TEM shows that the nanostar has many arms, varying from a few to over 30, whereby even the largest ones are found to have single-crystal structures. This strongly suggests that they are formed by a growth mechanism of the seed crystals and not by the aggregation of seed crystals, which should produce twinning planes. Due to the redn. reaction of ferricyanide by thiosulfate, the nanostars are found to have an activation energy, which is nearly 60% of that of the tetrahedral seeds themselves, both having the same PVP capping agent. This is undoubtedly due to the multiarms with edges, corners, and the presence of high indexed facets in the nanostar catalyst.

Recently a paper was published by Japanese authors in which they gave strong evidence confirming our previous proposal of the formation of Prussian Blue in the platinum nanocatalysis of the reaction between thiosulfate and Ferri-cyanide.

Training and Development:

Both Chris Tabor and Radha Narayanan have learnt the techniques of e-beam lithography, femtosecond laser technology and transmission electron microscopy and nanotechnology.

Dr Radha Narayanan who was trained and received her PhD with the support of this grant, has accepted a faculty position at the university of New Hampshire.

Ms Rachel Given who did research with us the past two summers was accepted in the graduate school at Berkeley, Stanford and Georgia Tech. She is coming to Georgia Tech to work on nanocatalysis.

The last year we were successful in attracting three young ladies to our graduate program. We also have been successful in accepting a female graduate student that did not pass the literature Exams and was asked to leave the program but we could tell that she is very talented in research. We helped her in trying the literature exams again. She has now passed this and is doing very creative research.

Christopher Tabor received his PhD in our group and was offered and accepted a postdoctoral position at the Air Force Research Laboratory at Dayton , Ohio

Outreach Activities:

1. Gave couple of public lectures on nanotechnology to two local companies.
2. Few months ago I was invited to talk to a retired professional club in Atlanta in a church.

3. Two females received their Ph D with the NSF support

4 Last summer, two REU AND ONE NNIN FEMALE STUDENTS RECEIVED THEIR RESEARCH summer TRAINING IN OUR GROUP.

5. This last summer, we accepted to train an REU student from Puerto Rico.

6. I gave a popular talk about Nano-technology to the annual meeting of the ACS Georgia section.

Journal Publications

Narayanan, R.; El-Sayed, M. A. "", 2007, submitted. (Invited Review Article), "The Nanocatalysis Revolution: Nanoparticle Stability, Catalytic Activity, and Recycling Potential", Top. Catal, p. , vol. , (2007). Accepted,

Susie Eustis and Mostafa El-Sayed, "Aspect Ratio Dependence of the Enhanced Fluorescence Intensity of Gold Nanorods: Experimental and Simulation Study", Journal of Phys. Chem. B, p. , vol. 109(39), (2005). Published,

Mahmoud, M.A.; El-Sayed, M.A., "Reaction of Platinum Nanocatalyst with the Ferricyanide Reactant to Produce Prussian Blue Analogue Complex.", . Journal of Physical Chemistry C, p. 17180, vol. 111, (2007). Published,

Mahmoud A. Mahmoud, Christopher E. Tabor, Mostafa A. El-Sayed,, "A New Catalytically Active Colloidal Platinum Nanocatalyst: The Multi-armed Nanostar Single Crystal", Journal of the American Chemical Society, p. 4590, vol. 130, (2008). Published,

Narayanan, Radha; El-Sayed, Mostafa A., ""Some aspects of colloidal nanoparticle stability, catalytic activity, and recycling potential.", Topics in Catalysis, p. 15, vol. 47, (2008). Published,

Tabor, Christopher; Narayanan, Radha; El-Sayed, Mostafa A, "Catalysis with transition metal nanoparticles in colloidal solution: Heterogeneous or homogeneous", Book Title: "Model Systems in Catalysis: From Single Crystals and Size-Selected Clusters to Supported Enzyme Mimics., p. , vol. , (2009). Accepted,

Mahmoud, M. A.; El-Sayed, M. A., "Comparative Study of the Assemblies and the Resulting Plasmon Fields of Langmuir-Blodgett Assembled Monolayers of Silver Nanocubes and Gold Nanocages", Journal of Physical Chemistry C, p. 14618, vol. 112, (2008). Published,

Narayanan, R.; El-Sayed, M. A., "Some Aspects of Colloidal Nanoparticle Stability, Catalytic Activity, and Recycling Potential", Topics in Catalysis, p. 15, vol. 47, (2008). Published,

Narayanan, R.; Tabor, C.; El-Sayed, M. A., "Can the Observed Changes in the Size or Shape of a Colloidal Nanocatalyst Reveal the Nanocatalysis Mechanism Type: Homogeneous or Heterogeneous?", Topics in Catalysis, p. 60, vol. 14, (2008). Published,

Narayanan, R.; El-Sayed, M. A., " Catalysis by metallic nanoparticles: the good and the bad", Chimica Oggi, p. 84, vol. 25, (2007). Published,

Tabor, C.; Narayanan, R.; El-Sayed, M. A., "Catalysis with Transition Metal Nanoparticles in Colloidal Solution: Heterogeneous or Homogeneous", Model Systems in Catalysis: From Single Crystals and Size-Selected Clusters to Supported Enzyme Mimics., p. , vol. book, (2009). Published,

Svetlana Neretina, Wei Qian, Erik C. Dreaden, Robert A. Hughes, John S. Preston, Peter Mascher, Mostafa A. El-Sayed,, "Plasmon Field Effects on the Nonradiative Relaxation of Hot Electrons in an Electronically Quantized System: CdTe-Au Core-Shell", nano-letter, p. 2410, vol. 8, (2009). Published,

Books or Other One-time Publications

Web/Internet Site**Other Specific Products****Contributions****Contributions within Discipline:**

1. In the field of colloidal nanotechnology, the synthesis of monodispersed sample is most important. Combining the E beam method and pulsed laser technique is a new technique to do so.

2. In the field of nanocatalysis, the important question now is where is the catalysis occurring, on the the nanoparticle surface or the nanoparticle reacts with one of the reactants forming complexes that can catalyze the reaction in solution. By spectroscopic studies we were able to detect these complexes in the solution and finally determine the exact reaction mechanism.

3. Not everyone has a TEM to determine the aspect ratio of gold nanorods. The method we developed, using an optical spectrometer, will be very useful.

Contributions to Other Disciplines:

1. Finding 1 Could be used in the semiconductor field as well.

2. The field of catalysis is important to many fields of chemistry and chemical engineering.

Contributions to Human Resource Development:

Susan Eustis, a bright young lady, is the one that developed the aspect ratio technique. She received an NRC fellowship at NIST.

Rachell Given, one of our brightest undergraduates did research with us last summer as well as the summer before. She is now going to graduate school and applying for an NSF fellowship.

Radha Narayanan who received her PhD with NSF support and will become a faculty member at the university of New Hampshire starting July 2008.

Contributions to Resources for Research and Education:

One of the graduated students, Radha Narayanan, is a minority and presently looking for an academic job. If she succeeds, she will help correct the distorted small number of female faculty in Academia.

Accepted a position at U. New Hampshire.

Similarly, Rachelle Givens who worked with us, is applying for graduate school and is interested in academic career.

She is coming to Georgia Tech to study Nano Catalysis after being accepted by U C Berkeley and Stanford.

Contributions Beyond Science and Engineering:

The two techniques developed could be commercialized.

Conference Proceedings**Categories for which nothing is reported:**

Organizational Partners

Any Book

Any Web/Internet Site

Any Product

Any Conference